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FORMATION OF THE CRYSTALLINE STRUCTURE OF A SILICON SURFACE IN ACTIVE MEDIA DURING POLISHING

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When surfactants are present in polishing compositions severe damage is done to the initial crystal structure of a very thin (tenths and hundredths of a micron thick) surface layer of the material (silicon) being processed and the deformation-strength properties of the material change as a result of the Rebinder effect. The use of active additives in polishing compositions, including unconventional ones, makes it possible to decrease the thickness of the damaged layer by a factor of 1.5 – 2, significantly increasing the polishing efficiency in the process.

Key words: silicon, polishing, Rebinder effect.

Silicon, widely used to make laser mirrors, solar batteries and other semiconductor devices, is difficult to machine.

Increasing the efficiency of finishing and polishing of silicon elements is a pressing problem of materials processing technology. Another important problem is improving the surface quality of articles (reaching the minimum micro-roughness with the smallest possible thickness of the damaged surface layer).

Polishing is usually done using a suspension of an abrasive powder in a dispersion medium. The abrasive particles, which effectuate plastic deformation and dispersion of the surface being worked, are not the only substances making polishing happen. Surfactants present in the dispersion medium change the deformation-strength properties of the surface being worked and thereby increase the surface quality of the article. This phenomenon is based on the Rebinder effect [1, 2].

In a previous work we found that surfactants selectively weaken interatomic bonds in the crystal lattice of ruby along definite crystallographic planes [3].

It was also shown that the active components of the polishing compositions have a large effect on the dispersion of the surface layer of ruby during fine abrasive machining [4].

The aim of the present work was to investigate the effect of surfactants in the polishing composition on the formation of the crystal structure of the surface of silicon plates and the increase in their machining efficiency. Polishing was done along the (111) plane.

Small quantities (1 – 2% of the mass of the dispersion medium) of active additives were introduced into the polishing compositions: halogen containing complex ester and fine aluminum powder. The time required to eliminate the micro-relief of the surface formed at the preceding stage of machining with larger abrasive grains, was chosen as the criterion for the efficiency of the polishing composition.

The crystal structure of the surface of the polished samples was studied by means of electron diffraction in reflection combined with layer-wise electrolytic etching of the silicon surface in a 10 : 1 mixture of nitric and hydrofluoric acids. The thickness of the etched layer was determined with a micro-interferometer and micro-profilograph relative to the initial (unetched) surface.

The diffraction patterns obtained from the surface of the silicon plates polished with ASM-1 diamond paste consisted mainly of diffuse halos corresponding to diffuse scattering of electrons from a strongly dispersed layer of silicon. The sizes of the crystallites in the dispersed layer, which are determined according to the half-width of the (511) line, were found to be 1 – 2 nm. The diffraction pattern was obtained in

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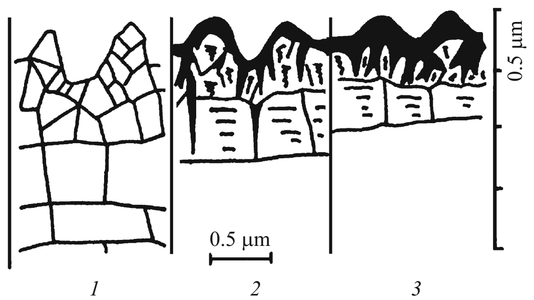

Fig. 1. Diagram of the structure of the damaged surface layer of silicon polished with different active additives in the polishing compositions: *1*) polishing with the based diamond paste ASM-1; *2*) ASM-1 paste with halogen containing ester; *3*) ASM-1 paste with added aluminum powder; light regions) crystallites formed as a result of the damage to the silicon single crystal; dark regions) intercrystallite layers of silicon, amorphized as a result of strong plastic deformation.

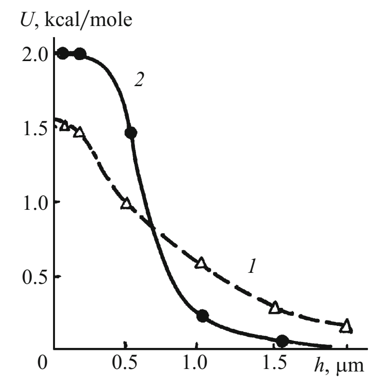

Fig. 2. Depth variation of the energy density U stored in the crystal lattice of the surface layer Si(111) machined by polishing compositions: *1*) ASM-1 base diamond paste; *2*) ASM-1 base diamond paste with an active additive.

a glancing beam, i.e., the angle between the electron beam and the surface studied was close to 0°.

As the angle between the electron beam and the surface of the sample increases from 0 to 4° and therefore as the probing depth increases, extended reflections appear against the background halo. The main smearing of the reflections is observed in the (111) direction, perpendicular to the surface of the sample. This is associated with the fact that lattice defects in the surface layer of the polished samples (including residual plastic deformations) are located in planes oriented parallel to the surface of the sample. This arrangement of the defects is explained by the anisotropy of the packing density of the atoms in the crystal lattice of silicon, which assumes its maximum value along the (111) planes.

As the polished surface of the silicon plates is etched, the background created by the electrons scattered diffusely from the amorphous phase decreases and the reflections from the single-crystal phase become sharper.

This can be illustrated by the scheme (Fig. 1) constructed according to the electron diffraction data. A unique feature of this scheme of the destruction of the single-crystal structure is the presence of amorphous material not only on the sample's surface itself (in the form of the Bailby layer) but also in the gaps between the slightly disoriented single-crystal grains. The depth and character of the distortions of the crystal lattice largely depend on the physical and chemical properties of the polishing composition.

To determine the effect of the active additives on the structure of the surface layer it is necessary to have a quantitative characteristic of the degree of damage to the crystal lattice of the machined material. One such characteristic is the change in the density of the energy U stored in the crystal lattice over the depth of the surface layer. To determine U the sizes and degree of deformation of the crystallites were calculated according to the smearing of the main reflections in the (111) and (224) directions. In addition the volume fraction of the amorphized regions was taken into account by performing photometric measurements on the (511) line and the (333) reflections for angle of incidence of the electron beam 1°. Knowing these parameters as well as the depth (20 – 40 nm) and direction (111) of probing it was possible to determine the energy density stored in the crystal lattice of the surface being studied. Layer-wise etching of the surface layers in combination with the electron diffraction studies made it possible to determine the distribution of the stored energy density over the depth h of the sample (Fig. 2).

The relative volume of the amorphized regions was determined on the basis of the ratio of the intensities of the (511) lines and (333) reflections. It was assumed in the calculations that the surface energy of the silicon is equal to approximately 2 J/m^2 [4], and about half of the interatomic bonds are broken on the intercrystallite boundaries [5].

Analysis of the electron diffraction patterns showed that the degree of damage to the initial single-crystal structure, characterized by the stored energy density U, depends on the physical and chemical properties of the active additives in the polishing compositions.

When an active additive is introduced into the polishing composition the destruction of the crystal lattice in a very thin surface layer increases as a result of the Rebinder effect. However, it is precisely in this layer, which is a pseudo-fluidized structure, that the elastoplastic deformations caused by abrasive working are localized.

Being subjected to severe damage the very thin surface layer of the machined material weakened by the influence of the surface-active medium localizes within itself excess deformations and thereby prevents the destruction of deeper layers, which is equivalent to thinning of the damaged layer.

When the indicated active additives are used in the diamond paste, the thickness of the damaged layer decreases by a factor of 1.5 – 2. At the same time the polishing becomes more efficient.

The fact that the aluminum powder, which initially was not as hard as the diamond particles, sharply intensified the

TABLE 1. Change in the Crystal Structure of Silicon Polished along the (111) Plane with Different Polishing Compositions to the Extent of Electrochemical Etching

Distance from the surface	Polishing composition		
	ASM-1 diamond paste	Diamond paste ASM-1 + halogen-containing ester	ASM-1 diamond paste + aluminum powder
0 – 5 nm	80% amorphous phase; 20% crystallites 1 – 2 nm in size	90% amorphous phase; 10% crystallites 0.5 – 1 nm in size	80% amorphous phase; 20% crystallites 10 nm in size
0.5 μm	50% amorphous phase; 50% slightly deformed single-crystal	70% crystalline blocks 10 nm in size; 30% crystalline blocks 20 – 40 nm in size	60% amorphous phase; 40% single crystal
1 μm	90% slightly deformed single crystal; 10% crystal monoblocks 20 – 40 nm in size. Texture relative to Si (111)	50% crystalline blocks > 100 nm in size; 50% Si(111) single crystal	Slightly deformed single crystal
1.5 μm	Si(111) single crystal. No Kikuchi lines	Si(111) single crystal. Kikuchi lines	Si(111) single crystal. Kikuchi lines
Increase of polishing efficiency with respect to ASM-1 paste	–	300%	100%

polishing of silicon attests not to mechanical (abrasive) but rather physical-chemical activation of polishing. This is associated with the fact that the aluminum at temperature 375°C forms with silicon a eutectic possessing much lower mechanical properties than pure silicon. The high local temperatures (up to 1000°C) in the work zone are a prerequisite for the formation of such a eutectic.

The high effectiveness of halogen-containing ester in this case is explained by the direct chemical interaction with silicon and by the formation, as a result of its mechano-chemical destruction, of short-lived and therefore the most active free radicals, which, being a kind of surfactant, weaken the machined surface and improve its machinability. Other components of the polishing composition can also be subjected to mechano-chemical destruction [6, 7].

The change in the crystal structure of the silicon polished along the (111) plane with different polishing compositions to the extent of the electrochemical etching is presented in Table 1.

The effect of the active additives on the increase of the polishing efficiency for silicon plates is shown in the lower part of the table.

CONCLUSIONS

Severe damage to the crystal structure of a very thin (tenths and hundredths of a micron thick) surface layer of the machined material (silicon) and a change in its deformation-strength properties occur as a result of the Rebinder effect under the action of surfactants.

It is precisely this pseudo-fluidized layer, acting like a lubricant, that localizes within itself the excess deformations and prevents the destruction of the crystal structure of deeper layers of the machined material, decreasing in this manner the thickness of the damaged layer formed as a result of polishing.

The use of active additives in the polishing compositions, including unconventional ones, makes it possible to reduce the thickness of the damaged layer by a factor of 1.5 – 2, and in the process increasing the polishing efficiency.

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